

THE RAMAN EFFECT IN CERTAIN ORGANIC COMPOUNDS

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ABSTRACT

The Raman spectra of the normal and iso forms of propyl ether, amyl ether, propyl propionate, butyl propionate, amyl propionate, and also methyl propionate have been measured. Certain characteristic frequencies remain unchanged throughout the series but other frequencies which appear singly in the normal forms are split into several frequencies in the iso forms, due to the rearrangement of the atomic groups. The Raman spectra have also been observed in the ortho, meta and para forms of chlorotoluene, cresyl methyl ether, nitrochlorobenzene and nitrotoluene. In addition to the characteristic frequencies which remain unchanged there are certain frequencies which consistently increase from the ortho to meta to para forms. Similar increases are noted in the infrared absorption spectra of the xylenes.

INTRODUCTION

DATA on the incoherent scattering of light, as first observed by Raman,¹ should give important information about the different modes of vibration and rotation of molecules and the energies associated with each of these modes of vibration and rotation. Hence a study of the Raman effect in organic molecules gives a means of advancing our knowledge of these molecules. Dadiou and Kohlrausch² and others have already shown that certain atomic groupings in organic molecules are definitely associated with frequency shifts observed in the Raman effect.

It is the purpose of this investigation to compare the Raman effect in certain normal forms of organic compounds with the Raman effect in the iso forms of these same compounds and to investigate the influence on the Raman effect of shifting the substituents from the ortho to the meta and to the para position in organic compounds.

EXPERIMENTAL

The design of the apparatus used follows that suggested by Wood³ and modified by Morris,⁴ except that four mercury arcs were used instead of one. The arcs were vertical, as was also the tube which contained the substance to be examined. The scattered light, after passing through a totally reflecting prism was focused on the slit of the spectrograph. The tube containing the liquid was about 25 mm in diameter and 12 cm long. A blast of air kept the liquid and the arcs cool. The spectrograph was a specially constructed, high-speed instrument, with lenses of 6 inch focal length and 2.5 inch aperture. There were two 60 degree glass prisms with faces 2.5 by 4 inches.

¹ Raman, *Ind. J. Phys.* **2**, 387 (1928).

² Dadiou and Kohlrausch, *Ber.* **63**, 251 (1930); *J. O. S. A.* **21**, 286 (1931).

³ Wood, *Phil. Mag.* **6**, 729 (1928).

⁴ Morris, *Phys. Rev.* **38**, 141 (1931).

TABLE I. (Cont.)

Substance Formula	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
n-propyl ether $C_3H_7-O-CH_2$	2929(9) (deh)	2975(9) (adeafh)	3073(1) (fh)	1737(7) (a)	2933(7) (aeh)	2980(7) (afh)	3115(1) (ah)
iso-propyl ether $(CH_3)_2CH-O-CH(CH_3)_2$	2906(7) (aeh)	2958(7) (aegh)	3145(3) (ef)				
n-butyl ether $C_4H_9-O-C_2H_5$	2933(9) (aeh)	2975(4) (eh)					
iso-amyl ether $(CH_3)_2CH(CH_2)_2O$	1138(1) (de)	1172(2) (ae)	1456(9) (ae)				
n-propyl propionate $C_3H_7-COO-CH_2CH_3$							
iso-propyl propionate $C_3H_7-COO-CH(CH_3)_2$							
n-butyl propionate $C_4H_9-COO-C_2H_5$							
iso-butyl propionate $C_4H_9-COO-CH_2CH(CH_3)_2$							
n-amyl propionate $C_5H_{11}-COO-C_2H_5$							
iso-amyl propionate $C_5H_{11}-COO-CH_2CH(CH_3)_2$							
methoxy propionate $C_3H_7-COO-CH_3$	1041(10) (abe)	1201(4) (ae)	1379(3) (ae)	1592(8) (ae)	2914(6) (ae)	3056(8) (ae)	
o-chlorotoluene $C_6H_4-Cl-CH_3$	1208(4) (ae)	1369(2) (ae)	1581(3) (ae)	2920(4) (ae)	3057(7) (aegh)		
m-chlorotoluene $C_6H_4-Cl-CH_3$	1596(6) (ae)	2921(2) (aeh)	3059(5) (adeifg)				
p-chlorotoluene $C_6H_4-Cl-CH_3$	1156(4) (ae)	1185(2) (de)	1236(7) (ade)				
o-cresyl methyl ether $C_6H_4-CH_3-OCH_3$	1445(4) (a)	1613(5) (a)	2920(5) (a)	1296(5) (ae)	1441(2) (ae)	1595(7) (ae)	2909(2) (af)
m-cresyl methyl ether $C_6H_4-CH_3-OCH_3$	1207(3) (ae)	1287(5) (ae)	1370(1) (ae)	1448(4) (ae)	1605(4) (ae)	2917(2) (aefgh)	
p-cresyl methyl ether $C_6H_4-CH_3-OCH_3$							
For the remaining compounds all Raman lines were excited by Hg 4358							
o-nitrochlorobenzene $C_6H_4-NO_2-Cl$	1374(10)	1604(5)	3052(2)				
m-nitrochlorobenzene $C_6H_4-NO_2-Cl$	3055(2)						
p-nitrochlorobenzene $C_6H_4-NO_2-Cl$	1604(6)	3054(3)					
o-nitrotoluene $C_6H_4-NO_2-CH_3$	1360(10)	1592(4)	2918(1)	3051(2)			
m-nitrotoluene $C_6H_4-NO_2-CH_3$							
p-nitrotoluene $C_6H_4-NO_2-CH_3$	1360(10)	1613(7)	2915(1)	3053(3)			

RESULTS

In Table I data are given for the compounds studied. The frequency shifts are given in wave numbers. If a frequency is *underscored* it means that that frequency appeared as an anti-Stokes line as well as a Stokes line. The number in parenthesis after each frequency is the intensity, estimated visually from the plates. The letters in parenthesis following the intensity indicate the mercury lines which gave rise to a Raman line corresponding to the particular frequency. The letters signify mercury lines as follows:

	Wave-length in A.U.	Wave number in cm^{-1}		Wave-length in A.U.	Wave number in cm^{-1}
a	4358	22938	e	4047	24705
b	4348	22994	f	3663	27290
c	4339	23038	g	3654	27354
d	4078	24516	h	3650	27388

DISCUSSION OF RESULTS

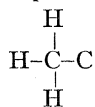
There are certain frequencies which remain unchanged throughout each of the series. These are the frequencies which are defined by Dadieu and Kohlrausch² as "inner" frequencies, and are due to molecular configurations which are present in each molecule. The vibration, which occurs in this configuration, is, therefore, very little affected by the remaining part of the molecule.

In the ethers and propionates under consideration, one of these constant frequencies is about 1450 cm^{-1} . This frequency has been assigned by Dadieu and Kohlrausch² and by Trumpy to the vibration of the group.

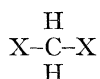


which occurs in each of the compounds. The C-H bond ordinarily gives frequencies in the neighborhood of 3000 cm^{-1} . That the CH_2 group can produce such a low frequency as 1450 cm^{-1} is explained by Dadieu and Kohlrausch by assuming that the hydrogen atoms vibrate at right angles to the direction of the linkage.

Another frequency, common to all the propionates, is 1735 cm^{-1} , approximately. Dadieu and Kohlrausch² have assigned this frequency to the C=O bond. The frequencies 2865 and 2929 cm^{-1} have been assigned by Dadieu and Kohlrausch to vibration of the group



and the frequency 2967 cm^{-1} to the linkage type



In the amyl and butyl propionates these three frequencies are not resolved but appear as a band.

TABLE II.

Substance	H -C- H	C=O	H H C-C H	H X-C-X H	NO ₂	C=C	C-H ali- phatic	C-H aro- matic
n-propyl ether	1446	—	2864	2931	—	—	—	—
iso-propyl ether	1453	—	2872	2929	—	—	—	—
n-amyl ether	1447	—	2853	—	—	—	—	—
iso-amyl ether	1449	—	2862	—	—	—	—	—
n-propyl propionate	1450	1737	2874	2933	—	—	—	—
iso-propyl propionate	1456	1737	—	2937	—	—	—	—
n-amyl propionate	1446	1732	—	—	—	—	—	—
iso-amyl propionate	1449	1731	—	—	—	—	—	—
n-butyl propionate	1450	1737	—	—	—	—	—	—
iso-butyl propionate	1456	1737	—	—	—	—	—	—
methyl propionate	1442	1735	—	2941	—	—	—	—
o-chlorotoluene	—	—	—	—	—	1592	2914	3056
m-chlorotoluene	—	—	—	—	—	1581	2920	3057
p-chlorotoluene	—	—	—	—	—	1596	2921	3059
o-dichlorobenzene*	—	—	—	—	—	1569	—	3066
m-dichlorobenzene*	—	—	—	—	—	1575	—	3072
p-dichlorobenzene*	—	—	—	—	—	1572	—	3061
o-xylene*	—	—	—	—	—	1594	2916	3043
m-xylene*	—	—	—	—	—	1597	2917	3042
p-xylene*	—	—	—	—	—	1618	2917	3040
o-cresyl methyl ether	—	—	—	—	—	1595	2909	—
m-cresyl methyl ether	—	—	—	—	—	1613	2920	—
p-cresyl methyl ether	—	—	—	—	—	1605	2917	—
o-nitrochlorobenzene	—	—	—	—	—	1374	1604	3052
m-nitrochlorobenzene	—	—	—	—	—	1369	1604	3055
p-nitrochlorobenzene	—	—	—	—	—	1360	1604	3054
o-nitrotoluene	—	—	—	—	—	1360	1592	2918
m-nitrotoluene	—	—	—	—	—	1364	1602	2920
p-nitrotoluene	—	—	—	—	—	1360	1613	2915
Average Values	1450	1735	2865	2932	2969	1364	1590	2918
								3054

* From Dadiou and Kohlrausch, J.O.S.A. **21**, 286 (1931).

In the ortho, meta and para group there is a frequency 3050 cm^{-1} which is present in each substance except cresyl methyl ether and which has been assigned by Dadiou and Kohlrausch² to the aromatic C-H bond. They have assigned the frequency 2918 cm^{-1} to the aliphatic C-H bond and the frequency 1600 cm^{-1} to the C=C bond. Ganesan and Venkateswaran,⁶ as well as Dadiou and Kohlrausch, have assigned the frequency 1364 cm^{-1} to the nitro group, NO₂.

Comparison of normal and iso forms

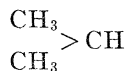
The molecules of the normal forms of ethers and propionates are supposed to consist of chains and in the iso forms these chains are split at one or both ends. Any difference in the Raman spectra ought to be explained, therefore, in terms of this rearrangement of the parts of the molecules.

In n-propyl ether there is a frequency 874 cm^{-1} which may be due to vibration of the group CH₃-CH₂. In the iso form this frequency is split into four frequencies: 791, 848, 903 and 930 cm^{-1} . This splitting must come from

⁵ Trumpy, Zeits. f. Physik **62**, 806 (1930).

⁶ Ganesan and Venkateswaran, Ind. J. Phys. **4**, 195 (1929).

the rearrangement of the groups in the split chain. A possible source of these frequencies is the group



This more complex arrangement would be expected to have a greater number of possible vibration frequencies than the simpler group CH_3-CH_2 . There is also a corresponding increase in the number of frequencies in the iso form as compared to the normal form in amyl ether and propyl propionate. (Fig. 1.) The results for amyl and butyl propionate are not satisfactory because of the large amount of continuous spectrum and the weakness of the lines.

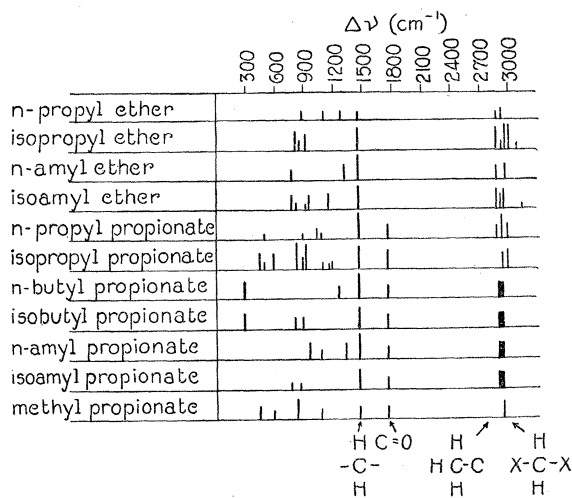


Fig. 1. Raman frequencies of normal and iso forms, showing the more complex spectra of the iso forms.

Comparison of ortho, meta and para forms

In these compounds there is a large number of frequencies, between approximately 150 and 1300 cm^{-1} , which have not been assigned to a particular vibrator. While these frequencies do not remain constant from one compound to another, yet there is a regularity in the shifts of some of them. (Fig. 2). In each case the smallest, and usually the two smallest frequencies increase progressively from the ortho to the para forms of the compound. But in addition to these smallest frequencies there are larger frequencies which have this same regular increase. Fig. 3 shows the frequencies which thus shift.

It is important to notice that these same shifts occur in the infrared spectra of ortho, meta and para-xylene. Coblenz⁷ calls attention to the regular shifting of two infrared bands in o, m and p-xylene. These two bands, at about 9.7 and $13.4\ \mu$ are shown in Fig. 3 under *infrared*. It will be seen from Fig. 3 that there is a Raman frequency which corresponds to each of these particular infrared frequencies. (The dotted Raman frequencies were not observed by Dadiou and Kohlrausch). There are also two additional Raman frequencies

⁷ Coblenz, "Investigations of Infrared Spectra," Carnegie Institution of Washington Publication 35 (1905).

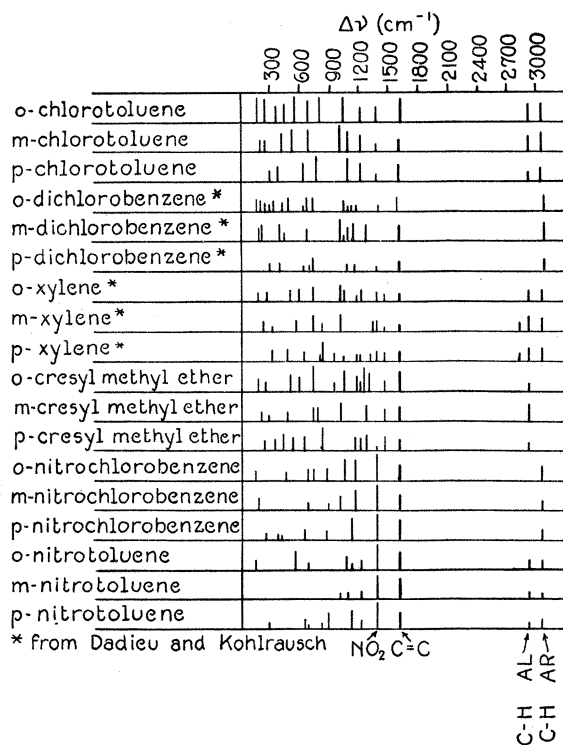


Fig. 2. Raman frequencies of ortho, meta and para forms, showing characteristic frequencies and shifting of certain other frequencies.

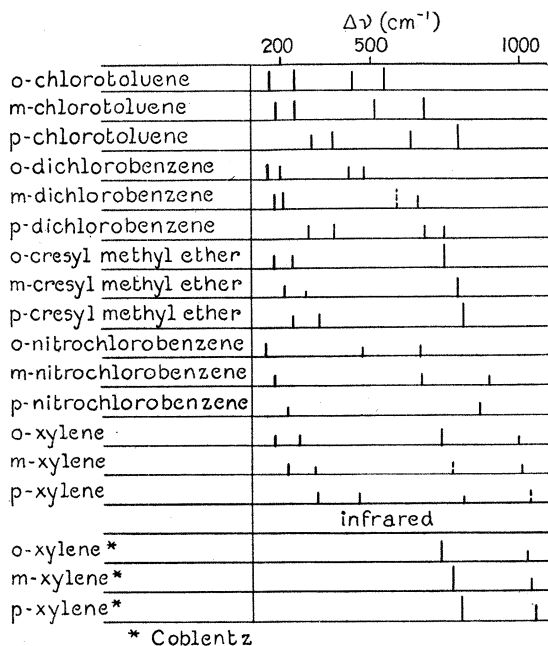


Fig. 3. Increase in frequencies from ortho to meta to para forms.

which show the same sort of shift but which lie outside the region studied by Coblenz. For xylene, then, the Raman spectra show the same shifts which occur in the infrared spectra, but in addition the Raman spectra show this same sort of shift in other frequencies which have not yet been observed by infrared methods.

In Fig. 3 the frequencies which show shifts similar to those of the xylene frequencies are plotted. Nitrotoluene is not included because of the failure to observe the smaller frequencies in m-nitrotoluene.

Comparison with infrared data

A comparison between the Raman spectrum and infrared spectrum of a substance shows in general that there are certain frequencies common to both spectra and other frequencies which appear only in the Raman spectrum or only in the infrared spectrum. In Table III the wave-lengths common to both

TABLE III.

Substance	Wave-length in μ		Substance	Wave-length in μ	
	Raman	Infrared*		Raman	Infrared**
o-nitrotoluene	3.43	3.42	methyl propionate	3.40	3.4
	6.26	6.25		5.76	5.8
	7.35	7.5		6.94	6.9
	8.56	8.4		9.3	9.2
	9.4	9.36		12.0	11.9
p-nitrotoluene	3.28	3.23	iso-amyl propionate	5.76	5.9
	3.43	3.43		6.94	7.0
	7.35	7.5		12.2	12.5
	8.88	8.65		13.0	13.1

* Coblenz, "Investigations of Infrared Spectra," Carnegie Institution of Washington Publication 35 (1905).

** Weniger, Phys. Rev. **31**, 388 (1910).

spectra are given for the four compounds for which infrared data were available. There are other frequencies in each spectrum which are found only in that spectrum. These results are in accord with the theoretical treatment of Ganesan and Venkateswaran.⁶ They have pointed out that an infrared absorption band involves only two energy levels and a transition must be permissible between these two levels, while a Raman frequency involves three levels, the initial and final and a third level. Hence the presence of an infrared band depends on the possibility of a transition between two given levels, while the occurrence of a Raman frequency depends on the presence of a suitable third level, and these two conditions may be quite independent.

Continuous spectrum

Every Raman spectrum contains a certain amount of continuous background. One method for removing most of this continuous background in certain cases has been reported in the Physical Review **38**, 374 (1931).

In conclusion the author wishes to express his appreciation to Professor Alpheus W. Smith for suggesting the problem and for his advice and assistance in the work. He is also indebted to Dr. M. L. Pool for valuable suggestions and criticism throughout the course of the work.